Anal. Chem. **2002,** *74,* 2423−2427

The Sonogel-Carbon Electrode As a Sol−Gel Graphite-Based Electrode

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In this work, a novel sol−gel-based procedure to obtain solid carbon composite electrodes is proposed. The procedure is based on the use of sonocatalysis to apply high-energy ultrasound directly to the precursors; this way, ultrasonic cavitation is achieved so that hydrolysis with acidic water is promoted in the absence of any additional solvent and the time needed to get a unique phase is reduced drastically. The mix of sonogel with spectroscopic grade graphite leads to a new type of sol−gel electrode: the Sonogel-Carbon electrode. The amount of water, necessary for hydrolysis to occur, has been studied, as well as the sol pH value and the electrochemical behavior of the Sonogel-Carbon electrode in Britton−Robinson buffer. Mechanical renewal of the electrodes surfaces and background signal stability for at least 42 days have been also tested. We have carried out some tests to check the ability of the synthesized material to give electrochemical response when redox species are present in the background electrolyte. Mechanical and electrochemical studies indicate that the Sonogel-Carbon electrode shows good properties for use as an electrochemical sensor.

The employment of sol−gel chemistry to produce carbon-based conducting matrixes has received increasing interest in recent years.[1−5] The use of this type of procedure to find alternative materials to the ones typically used in solid electrodes must be explained in terms of a series of characteristics that points them out as plausible options. Advantageous features include high conductivity, relative chemical inertness, wide operational voltage window, good mechanical properties, physical rigidity, renewable surface, amenable chemical or biological modification, and stability in various solvents.[6,7] In addition, the procedure developed for the fabrication of the electrodes is easy; by simply adding graphite to the precursors solution, conductivity is conferred to it and the mixture is readily malleable, so that virtually any configuration can be obtained. Furthermore, there is also the opportunity to tailor the structures by controlling the chemistry of the sol−gel process, thus yielding materials with very different properties.[8] For instance, it is possible to prepare hydrophobic or hydrophilic surfaces by changing the type of silicon precursor in the sol−gel solution. Thus, when methyltrimethoxysilane is used, water is repelled so only the outermost section is active, whereas the use of tetramethoxysilane leads to hydrophilic materials.

The sol−gel process is a chemical synthesis technique that enables the possibility of preparing a wide variety of oxide compounds at far lower temperatures than conventional methods. It is a fusionless method for the synthesis of ceramic and organically modified ceramic materials.

Nowadays, there is evident interest in a new range of sol−gel-derived carbon-based electrodes, which are being developed and employed in electrochemical applications. In this paper, we propose a novel sol−gel-based procedure as a way to yield solid carbon composite electrodes. Classical procedures reported in the literature for the synthesis of acid-catalyzed sol−gel-based electrode materials include the addition of an alcoholic solvent to the initial precursor mixture to make it homogeneous (since the system is not miscible). The later evaporation of this component involves an inevitable marked reduction of the volume of the material, which is completely undesirable when solid electrodes are being prepared. Also, these procedures generally need more than 10 min of sonication in an ultrasonic bath for the hydrolysis reaction (and so the sol−gel process) to be initiated.

Our proposal is fairly different and is based on the use of sonocatalysis[9,10] to synthesize solid carbon composite materials for the preparation of electrodes. By means of sonocatalysis, high-energy ultrasound is applied directly to the precursors, and ultrasonic cavitation is achieved so that hydrolysis with acidic water is promoted in the absence of any additional solvent. Thanks to the phenomenon of ultrasonic cavitation, sol−gel reactions occur in a unique environment, leading to gels with special

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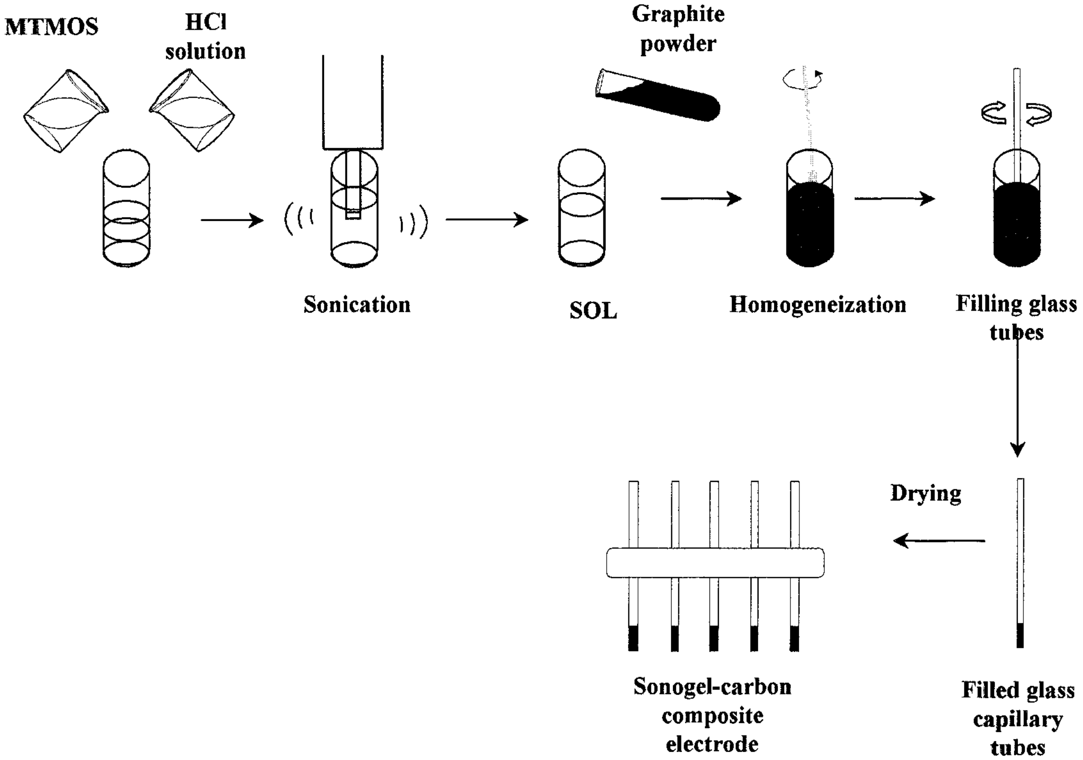

Figure 1. Scheme of the steps followed for the processing of the Sonogel-Carbon composite electrodes.

characteristics. These so-called sonogels are mainly of high density, with a fine texture and homogeneous structure. The mix of sonogel with spectroscopic grade graphite leads to a new type of sol−gel electrode: the Sonogel-Carbon electrode.[11,12]

EXPERIMENTAL SECTION

Reagents and Materials. Methyltrimethoxysilane (MTMOS) was from Merck (Darmstad, Germany) and HCl was from Panreac (Barcelona, Spain). Boric acid, orthophosphoric acid, acetic acid, and sodium hydroxide for the Britton−Robinson buffer solution were from Merck. All reagents were of analytical grade or higher and used as received without further purification. Graphite powder (spectroscopic grade RBW) was from SGL Carbon (Ringsdorff, Germany). Nanopure water was obtained by passing twice-distilled water through a Milli-Q system (18 MΩ·cm, Millipore, Bedford, MA). All analytes tested in this work were of analytical grade and were purchased from Merck, Fluka (Buchs, Switzerland), or Panreac.

Glass capillary tubes, i.d. 1.15 mm, were used as the bodies for the composite electrodes.

A carbon paste electrode and a glassy carbon electrode (both with a surface area of 7 mm^2 and purchased from Metrohm, Herisau, Switzerland) were used as working electrodes in some measurements. Carbon paste electrode was prepared as described previously.[13]

Instrumentation. All the electrochemical measurements were performed with an AutoLab PGSTAT20 (Ecochemie, Utrecht, The Netherlands) potentiostat/galvanostat interfaced with a personal computer, using the AutoLab software GPES for waveform generation and data acquisition and elaboration. The experiments were carried out in a single-compartment three-electrode cell, at room temperature (25 ± 1 °C), under nitrogen atmosphere. The counter electrode was a platinum wire, and a silver/silver chloride/3 M KCl electrode was used as the reference. The composite-filled glass capillary tubes were used as the working electrode.

A 600-W model, 20-kHz ultrasonic processor (Kontes) equipped with a 13-mm titanium tip was used. The ultrasonic processor was enclosed inside a sound-proof chamber during operation.

Scanning electron microscopy (SEM) studies were carried out on a JSM 820 instrument (JEOL, Japan) operating at 30 keV and equipped with a Microanalyzer AN/10000.

Cyclic voltammetry (CV) and also differential pulse voltammetry (DPV) were the electrochemical techniques applied to study the behavior of the Sonogel-Carbon electrodes. CV scans were made at 100 mV·s^{-1} in the range −0.8 to +1.1 V. DPV was carried out from 0 to ±1 V, depending on the nature of the process to be studied (reduction or oxidation). Other instrumental parameters for DPV were as follows: pulse amplitude ±100 mV, pulse repetition time 0.2 s, scan rate 25 mV·s^{-1}, and a pretreatment at 0 V for 2 min if it was required.

Electrode Preparation Procedure. To prepare the sonosol, the general procedure was as follows (Figure 1): 500 μL of MTMOS was mixed with various volumes of HCl solutions of suitable concentrations, according to the amount of water required but maintaining the quantity of the catalyst (HCl). This mixture was then insonated for 5 s (energy dose 0.083 kJ·mL^{-1}). Next, a fixed amount of graphite powder, 1 g, was added and homogeneously dispersed in the sonosol obtained. After several minutes,

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the resulting material acquired enough consistency and the glass tubes were filled, leaving a little extra mixture sticking out of the glass tube to make easy the ulterior polishing step. After 20−24 h, depending on the proportion of H_2O, the Sonogel-Carbon composite electrodes had got hardened and, therefore, structured. Adherence between the developed material and glass was excellent. Before use, the electrodes were polished with No. 1200 emery paper to remove extra composite material and wiped gently with weighing paper. Electrical contact was established by inserting a copper wire.

RESULTS AND DISCUSSION

As the Experimental Section indicates, to prepare the sonosol, MTMOS and HCl are put into a glass receptacle of appropriate dimensions and shape. This precursor mixture is composed of two phases. To obtain the sonosol, the sol−gel process has to be initiated and this involves promoting the hydrolysis (what is experimentally known because a unique phase is observed). With the high-power ultrasonic processor, the mixture is subjected to the phenomenon of ultrasonic cavitation, by which a very close contact between the two immiscible phases is reached (vibrations create pressure waves in the liquid and this action forms millions of microscopic bubbles which expand during the negative pressure excursion and implode violently during the positive excursion). Unlike the case where an ultrasonic bath is used, the precursor mixture is locally insonated; thus, loses of energy are not significant, and the use of a suitable beaker containing water is always advisable to avoid getting the glass too warm and, therefore, risk its shattering. To do the insonation correctly, the tip of the probe must be just contacting the superior surface of the mixture (only ~1 mm of length must be introduced).

By applying ultrasonic cavitation to favor the sol−gel process to begin, we avoided the use of alcoholic solvent and reduced drastically the time needed to get a unique phase. As explained in the introduction, the use of an alcoholic solvent involves a reduction of volume not good for the preparation of solid electrodes. Also, whereas sonication times of ~10 min or more are necessary when an ultrasonic bath is used to elaborate gels, we have achieved a reduction from hours or minutes to several seconds. From the beginning, the mixture was insonated for 5 s (dose of energy of 0.083 $kJ\cdot mL^{-1}$) to promote cavitation and thus hydrolysis. Greater doses of energy up to 12 times higher were tested in order to study changes in the properties of the material. However, no improvement was obtained with the increase of supplied energy and, thus, with the increase of the time of insonation.

After reviewing the literature, we did not find any references dealing with the application of this system to prepare carbon ceramic electrodes (CCEs), so we consider this research to be the first in describing the by us-called Sonogel-Carbon electrodes.[11]

On the other hand, it has been reported that there is a possibility of increasing the cathodic range of measurements when carbon composite electrodes are used by passing nitrogen through the bulk of the electrodes before or during use.[6] The conduction of this inert gas across the material seems to eliminate the oxygen located in the highly porous structure, whose presence results in a reduction of the cathodic electroactive field achieved with the composite electrode. Our electrodes, made following a fairly different method, did not show significant improvements after being subjected to the procedures described in the literature, probably due to a low oxygen content, and they provided wide ranges of electroactivity without previous treatment.

Table 1. Observed Charging Capacity of Different Sonogel−Carbon and Carbon Electrodes in Britton−Robinson Buffer of pH 4.5 (Scan Rate, 100 $mV\cdot s^{-1}$).

graphite electrode type	C_{obs} ($\mu F\cdot cm^{-2}$)
carbon paste	496
glassy carbon	642
CCE (MTMOS/H_2O molar ratio)	
1:1	5913
1:3	211
1:1.5	28

For the first preparation, a 1MTMOS/3H_2O molar ratio and a pH sol value of ~1.5 were used. This attempt resulted in a composite material with good mechanical properties in which the graphite particles were perfectly retained within the silica network.

Influence of the Amount of Water. The presence of water is necessary for hydrolysis to occur. However, in the condensation reaction, water is formed as a product. Thus, if we would want to establish the appropriate quantity of water needed according to the silane used, this contribution should be taken into account. The stoichiometric amount of water would be determined at first by the alkoxide used. However, due to the condensation reaction, the water necessary will not be the correspondent to the stoichiometry but less. Some authors have taken this to the point of considering ambient humidity as an extra supply of water if needed, thus not looking at the stoichiometry at all.

In this work, 1:3, 1:1.5, and 1:1 MTMOS/H_2O molar ratios were tested. During the preparation of the composite materials, an increase of viscosity was easily observable as the proportion of water decreased; with regard to the mechanical properties, those materials with 1:3 and 1:1.5 ratios were found to be rigid and strong, unlike the 1:1 ratio, which turned out to be fragile and easily breakable. Also, for the 1:1 ratio, when the wire was pushed, the composite material moved easily along the glass tube; even a few days later, the mechanical properties were still the same. However, the part of the material close to the base of the tube and in direct contact with air was hard. This seemed to indicate that air humidity may not be enough as a supply of water if needed. Thus, after similar periods, suitable results are obtained for 1:3 and 1:1.5 ratios but not for the 1:1 ratio.

To evaluate the behavior of these composites as electrode materials, cyclic voltammograms were carried out in Britton−Robinson buffer of pH 4.5. The corresponding values of experimental observed capacity, a parameter defined as $C_{obs} = i/\nu$, where i is the average anodic and cathodic current density and ν is the scan rate (100 $mV\cdot s^{-1}$), were obtained. In these calculations, those parts of the voltammograms where faradaic intensities prevailed upon capacitive intensities were not considered.[6]

In Table 1, C_{obs} obtained for these composite materials and also for other graphite electrodes (carbon paste and glassy carbon) are included. An extremely high value of C_{obs} for a 1:1 molar ratio can be noticed; this reveals a high contribution of charging currents to the background current for this molar ratio under the conditions used. In contrast, C_{obs} values for 1:3 and 1:1.5 ratios

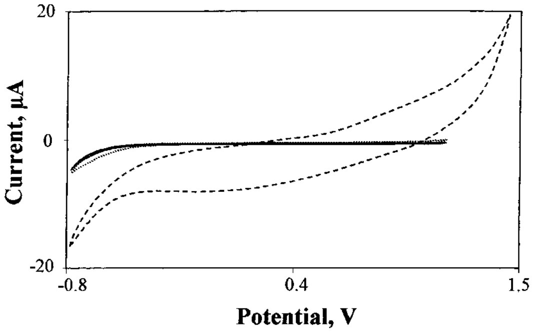

Figure 2. Cyclic voltammograms obtained with several electrodes with different proportion of water: 1MTMOS/1H_2O molar ratio (- - -), 1MTMOS/1.5H_2O molar ratio (—), 1MTMOS/3H_2O molar ratio (···). Scan rate, 100 mV·s^{-1}. Reference electrode, Ag/AgCl (3 M KCl).

are lower and closer together; furthermore, values for carbon paste and glassy carbon electrodes are fairly higher than that obtained for 1:1.5. These data are in correspondence with the cyclic voltammograms in Figure 2. As can be seen, whereas the voltammograms for the 1:3 and 1:1.5 molar ratios are clearly similar, the one for 1:1 ratio is fairly worse. Then, we decided to carry out SEM for the 1:3 and 1:1.5 ratios, which showed good features to be used as electrodes; the 1:1 molar ratio was not examined as it did not show suitable mechanical properties. The SEM pictures clearly showed a separation between the composite materials and the glass tube for the 1:3 ratio, whereas separation does not appear for 1:1.5 ratio. Looking at the whole of these differences, the 1:1.5 molar ratio was considered to be the most appropriate to use for the composite as electrode material.

The background current of graphite electrodes is contributed to by double-layer charging and surface faradaic reactions involving surface groups. For a ceramic carbon electrode obtained by sol–gel processes (not by sonocatalysis), a C_{obs} value of 90 μF·cm^{-2} was reported in the literature;[6] this result reveals a better behavior of the Sonogel-Carbon electrode for the optimum molar ratio (1MTMOS/1.5H_2O), for which a C_{obs} value of 28 μF·cm^{-2} was obtained (Table 1).

Next, double-layer capacity was calculated for a 1:1.5 ratio. This was done by making cyclic voltammetry scans at different scan rates in the range 0.005–0.1 V·s^{-1} and plotting average values of anodic and cathodic density currents for each scan rate versus them. The result is a line with a slope of 198.6 μF·cm^{-2} ($r^2 = 0.999$), which is the value of the mentioned parameter for the composite electrode under the established conditions.[14,15]

Other Relevant Parameters. The materials synthesized previously were developed with a sol pH value close to 1.5, giving good general behavior mainly for 1:3 and 1:1.5 ratios. That value of pH seemed to be appropriate, and also in the literature. fairly acid conditions are often recommended[1] to elaborate solid and compact electrode materials, since less acidic conditions provide graphite powder covered by silica. More acidic conditions were also assayed, but the mechanical properties of the obtained materials were poor. Consequently, we continued using a sol pH value close to 1.5.

The effect of varying the pH of the Britton–Robinson buffer on the background signal given by the sonogel–carbon composite electrodes was also studied. Figure 3 shows how the cyclic voltammogram varies in the range pH 2–10. The signal stays practically the same in the intermediate range of pH (4–8). Major changes are observed in the area close to the most positive potentials, whereas not significant variations are seen in the opposite area. The presence of a peak can be noted close to 0.4 V in the oxidation scan for pH 2, which quickly disappears when the pH increases. However in HCl/KCl media at pH values of 1.2 and 2.4, the peak is not present. We believe this peak could be attributable to some type of interaction at this pH value between the media and the material of the electrode when Britton–Robinson buffer is used, but this interaction does not appear for other electrolyte supports.

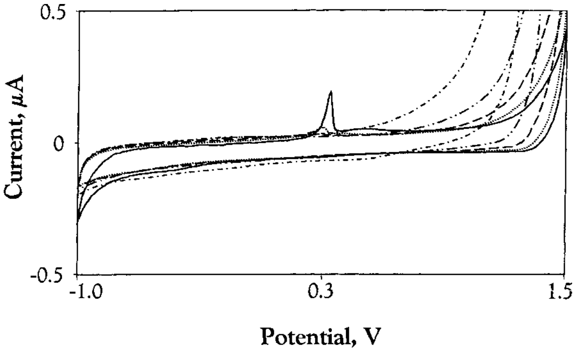

Figure 3. Cyclic voltammograms for different pH values of the Britton–Robinson buffer: pH 2 (—), pH 4.4 (···), pH 6.1 (– –), pH 8.3 (– · · –), and pH 10 (– · · –). 1MTMOS/1.5H_2O molar ratio. Scan rate, 100 mV·s^{-1}. Reference electrode, Ag/AgCl (3 M KCl).

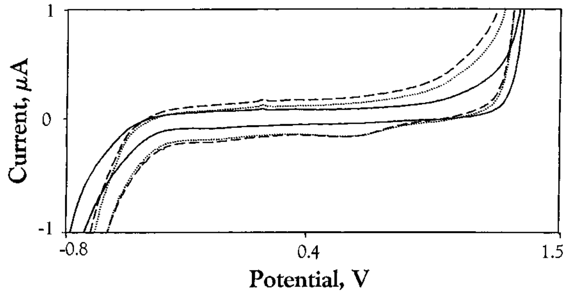

Figure 4. Cyclic voltammograms in Britton–Robinson buffer at pH 4.5 after mechanical renewal of the electrodes surfaces: first use (without mechanical renewal) (—); first mechanical renewal (···); second mechanical renewal (- - -). Scan rate, 100 mV·s^{-1}. Reference electrode, Ag/AgCl (3 M KCl).

Mechanical renewal of the electrode surfaces caused a certain variation in the signal as can be seen in Figure 4. After mechanical renewal, the electrode shows a high background current and a decrease of anodic and cathodic operational ranges. The rough surface of this sort of electrode, and their heterogeneous composition due to the graphite dispersed in the sol–gel matrix, must be taken into account in order to justify the small variations caused by this renewal method. Usually, authors underline the advantages of this type of renewal, but when a redox species is being analyzed, many authors use chemical or electrochemical renewal since the mechanical way gives high relative standard deviations in the signal intensities obtained for the analyte (generally about 10–15%).

On the other hand, evaluation of the variation of the cyclic voltammograms corresponding to three electrodes revealed an

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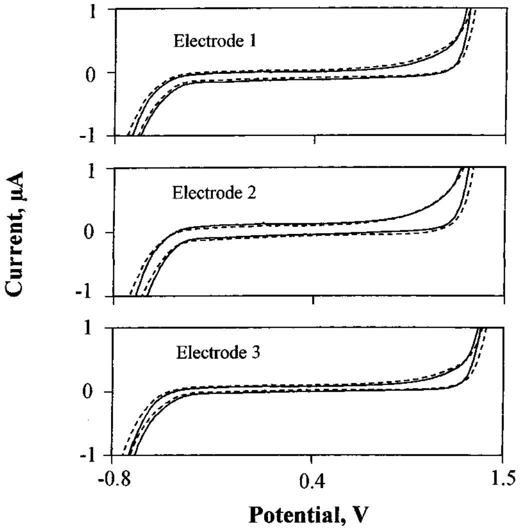

Figure 5. Stability of the electrodes. Cyclic voltammograms obtained from three electrodes in Britton−Robinson buffer at pH 4.5 after 42 days from their preparation: first use (24 h) (- - -); after 42 days (—). Scan rate, 100 mV·s^{-1}. Reference electrode, Ag/AgCl (3 M KCl).

excellent background signal stability after a long time (at least 42 days), as shown in Figure 5. All the electrodes showed similar voltammetric signals, and the same anodic and cathodic operational ranges.

Responses for Different Species. Although this work was focused on the development of the new procedure to make sol−gel graphite composite electrodes, we carried out some tests to check the ability of the synthesized material to give electrochemical response when redox species are present in the background electrolyte. With this aim, differential pulse voltammetry was used as the measurement technique.

We have found out that the material itself is able to give a response for a wide group of organic compounds of different nature and also for some inorganic metallic ions. Well-defined peaks can be clearly observed for several compounds (picric acid, 2-methyl-4,6-dinitrophenol, 2,4-dimethylphenol, pentachlorophenol, 2,4,6-trichlorophenol, 4-chloro-3-methylphenol). In this case, we also applied an electrochemical pretreatment consisting of maintaining a potential of 0 V for 2 min before taking the measurement. In all cases, the peak height increased (in different proportion depending on the compound). This fact seems to indicate that the use of electrochemical pretreatments prior to measurements might be a way to improve the sensitivity of the measurements. This behavior has already been extensively probed by our research group for the case of carbon paste electrodes, for which the adsorption of organic species has been demonstrated to take place onto the electrode surface;[16,17] the peak potentials of the signals obtained with the Sonogel-Carbon electrode are similar to those obtained with carbon paste electrodes. The electrochemical signal given by the analyte could not be eliminated by gently rinsing; therefore, mechanical or electrochemical renewal is needed to remove the adsorbed species from it.

In the case of metallic ions, different signal intensities and resolution were obtained for Cu(II), Pb(II), Zn(II), and Cd(II); the same behavior with respect to peak potentials has been found for these species at carbon paste electrodes. No evident signals were observed for Ni(II), CrO_4^{2-}, and Cr(III) under the conditions we used in these first tests. For Cd(II), two further tests were carried out. The first consisted of succesive additions of the metal, which achieved an excellent peak height/concentration ratio. In the second test, an ASDPV was run at an accumulation potential of −1.5 V for 120 s and a rest period of 20 s. In this case, the result was a signal 3−4 times higher and better defined than that obtained by DPV for the same concentration of Cd(II). This indicates the ability of the Sonogel-Carbon electrode to electrochemically accumulate certain metals, which is promising for future applications.

CONCLUSION

The application of sonocatalysis to a sol−gel process yields a material with special characteristics, and with the incorporation of graphite, we make a new type of electrode. By means of this experimental procedure, we avoid the use of alcoholic solvent and can reduce drastically the time needed to get a unique phase. The electrodes obtained do not need pretreatment to increase cathodic range, because they provided wide ranges of electroactivity without previous treatment. By controlling several fabrication parameters, we obtained a material with better characteristics to be introduced in the glass tubes, and the improvement of electrochemical behavior gives as a result a stable background baseline.

Due to the stability of the electrode, and the responses obtained for different organic and inorganic species, the Sonogel-Carbon electrode shows excellent properties to be used as electrochemical sensor.

ACKNOWLEDGMENT

The authors are grateful to the Ministerio de Ciencia y Tecnología of Spain and to the European Community (Project BQU2000-0455) for financial support.

Received for review July 10, 2001. Accepted February 14, 2002.

AC010782U

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